

Chemical effect on resonant inelastic *L* x-ray emission spectra in Cr compounds

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ABSTRACT

We have measured and analysed the resonant enhancement of photo-emission in the energy region of the Cr 2p threshold on Cr compounds using tunable synchrotron radiation. The Raman scattering peak is resonantly enhanced at excitation energies corresponding to Cr 2p absorption peaks. The x-ray absorption and emission spectra (XAES) of Cr(VI) are very different from those of Cr(III). The difference by the resonant photo-emission may be attributed to the effect of the covalency in bonding. Moreover, it is followed that XAES are very sensitive to ligand environment in Cr compounds and relatively insensitive to metal oxidation state, as Grush *et al.* suggested in Mn complexes [7].

KEYWORDS: Resonant; Soft X-ray; Emission; Fluorescence; Absorption; Transition metal; Chromium compounds.

INTRODUCTION

It was investigated by some workers [1-3] that the $K\alpha/K\beta$ x-ray intensity ratios for chemical compounds of Cr and Mn elements with tetrahedral symmetry were larger than those with octahedral symmetry. It is necessary to carry out further the studies of the chemical effect for L-x-ray spectra so as to elucidate the valence electronic structures of the 3d compounds.

There are three L subshells and the vacancy produced by the primary ionization process can move between subshells through Coster-Kronig transitions. In the vicinity of the absorption edges strong emission components, which are actually multiple-ionization satellites, can be misinterpreted as part of the parent emission band. This fact indicates that for the study of the L-x-ray emission spectra, it is absolutely required to tune the energy of the incident photons and excite each subshell selectively.

Much effect has inquired into using x-ray absorption spectroscopy (XAS) for the investigation [4-6]. The benefit of using soft x-rays to study 3d transition metals is the longer core hole lifetime of the L-edge transitions which occur in this region, compared to the corresponding K-edges in the hard x-ray regime. This decrease in the linewidth leads to better-resolved features in the spectra; that is, the resonant emission phenomenon involves the excitation of core electrons to a localized, empty state. If the core hole lives long enough, the electron may recombine with the core hole and subsequently emit a photon. A resonant feature is observed only if a localized unoccupied state exists. Thus selective excitations to the localized state provide an important opportunity to study the localized states.

Grush *et al.*[7] have recently showed that L-edge x-ray absorption spectroscopy is a sensitive probe of the oxidation and spin state of metal sites and soft x-ray fluorescence very sensitive to ligand environment and relatively insensitive to electronic geometry and metal oxidation state in Mn complexes.

In the present study we investigate the emission spectra of Cr compounds in the energy region of L-subshell absorption edges with Total Electron Yield method in BL 6.3.2 to elucidate the *d* character effect in the chemical binding.

EXPERIMENTAL

Soft x-ray absorption experiments were performed on Beamline 6.3.2 at the Advanced Light Source. This is a bend magnet beamline with a Hettrick-Underwood type monochromator capable of high resolution, as has been previously described [8]. A 1200 l/mm grating with an exit slit of less than 20 microns resulted in a resolving power ($E/\delta E$) of better than 1200 at the Cr L-edge.

The absorption was monitored by collecting the total current from the sample as a function of exciting energy. The incident intensity (I_0) of the x-ray beam was recorded as the current from either a gold mesh in the beampath or refocusing mirror. Spectra were recorded over a 60 eV range with a step size of about 0.1 eV. The spectra were divided by I_0 . All samples were finely powdered and identified by x-ray diffraction method, respectively. Both spectra have a 9.2 eV separation between L_3 and L_2 , in spite of the differences in geometry and ligand. The Cr (VI) spectra occur at 1.7 eV higher than the corresponding Cr (III) spectra, are much sharper, and decrease in broadness with increasing oxidation state has been observed in Cr compounds (Fig.1 and Table 1). Large differences in the ligand coordination can cause changes in electronic geometry and spin state which are often readily observable in the absorption spectra. The sample slide was then mounted perpendicular to the incoming x-ray beam.

Soft x-ray fluorescence spectra were recorded on Beamline 8.0 at the Advanced Light Source. This is an undulator beamline with a spherical grating monochromator, as has been previously described [9]. A 925 l/mm grating was used to monochromatize the excitation energy for these measurements. The incident beam intensity was monitored as the current from a gold mesh in the beampath.

The soft x-ray fluorescence end station [9] consists of a Rowland circle - type emission spectrometer with a fixed 100 micron entrance slit and a 1500 l/mm grating mounted on a 10 m Rowland circle. The x-ray fluorescence is refocused onto a multichannel plate area detector which enables the entire emission spectrum to be obtained without scanning the detector. Samples for emission measurements were finely powdered, pressed into pellets, and mounted in the chamber at 22 degree to the incoming beam.

Table 1 Cr $L_{2,3}$ peaks in Cr compounds

Compound	L_3 [eV]	L_2 [eV]	$L_2 - L_3$
Cr atom	574.5	583.7	9.2
Cr metal	575.8	585.0	9.2
Cr ₂ O ₃	575.8	585.0	9.2
FeCr ₂ O ₄	575.8	585.0	9.2
K ₂ Cr ₂ O ₇	577.5	586.7	9.2
Line	$L\alpha$	$L\beta$	
	573	583	10

RESULTS

The soft x-ray absorption and emission spectra of two oxidation state pairs are shown in Fig. 2. The Cr centers in Cr(VI) and Cr(III) have oxygen ligands with tetrahedral and octahedral geometry, respectively. In both cases, the x-ray absorption spectrum of Cr(VI) is strikingly different from that of Cr(III) as seen in Figures 1a. The L_3 peak occurs at 575.8 eV and 577.5 eV for the Cr(III)₂O₃ and K₂Cr(III)₂O₇. The appearance of the $L\alpha$ and $L\beta$ spectra to the ligand environment is shown in Figure 2. Cr L-emission spectra were recorded for Cr compounds. In the case of the Cr compounds with oxygen ligands: Cr metal, Cr(III)₂O₃, FeCr(III)₂O₄, Cr(IV)O₂, and K₂Cr(VI)₂O₇ the $L\alpha$ and $L\beta$ peaks maintain similar energy position for the same oxidation state. No difference in broadness was observed for any of the ligands in the $L\alpha$ region.

The observed spectra will be compared and interpreted with DV-X α theoretical calculations to clarify valence electronic structures of the compounds and the calculations are currently in progress.

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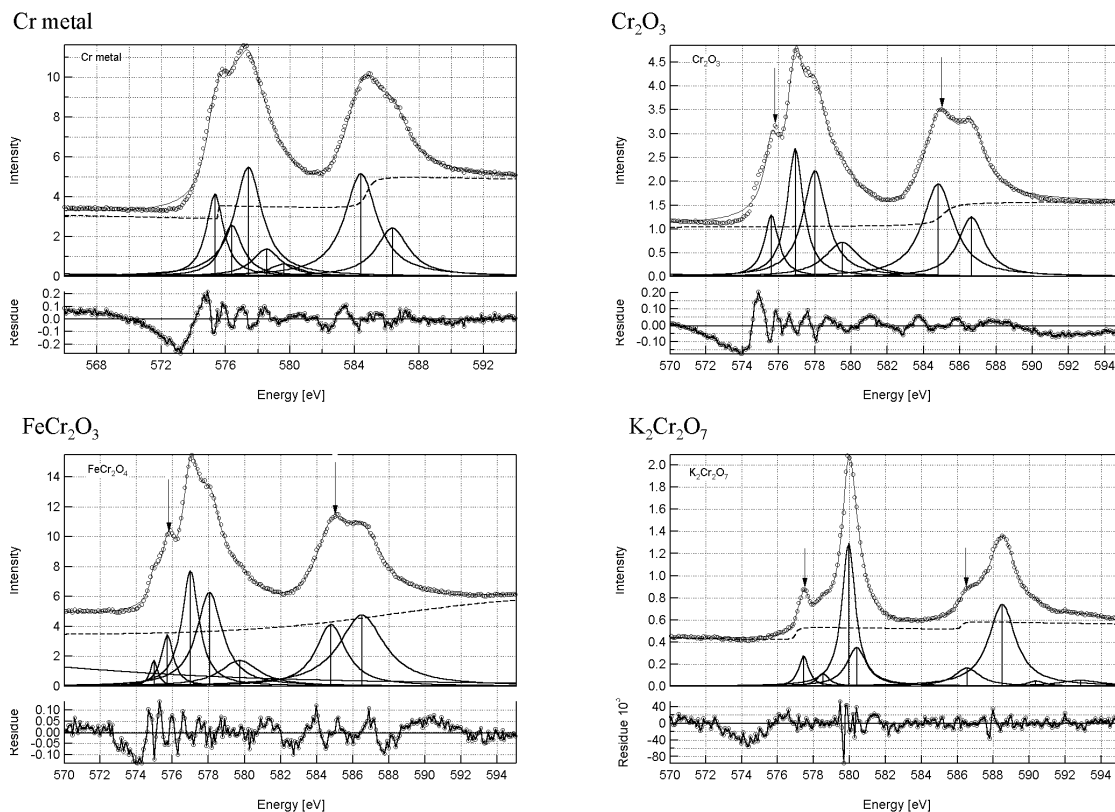
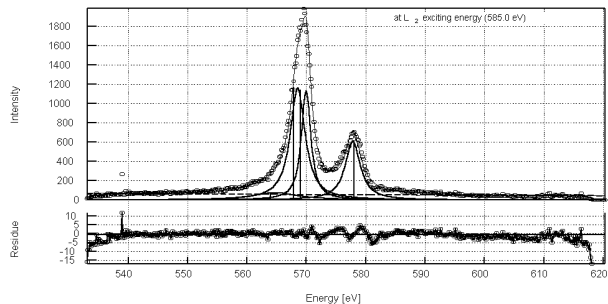
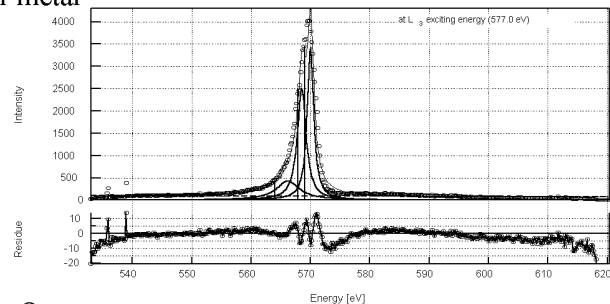
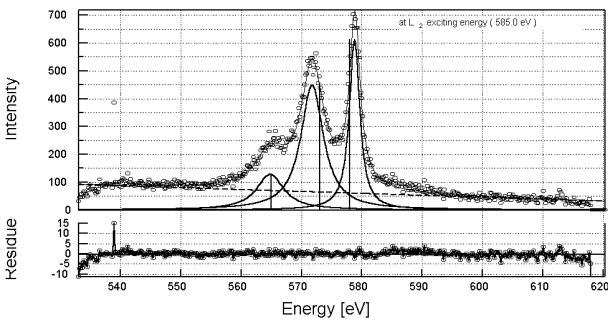
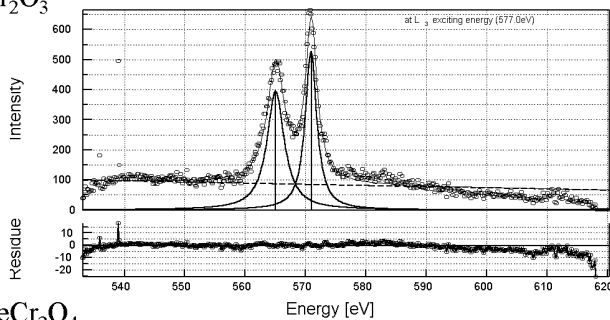


Figure 1. The Cr $L_{2,3}$ absorption spectra for the Cr compounds. The arrows on the absorption spectra indicate excitation energies used for fluorescence

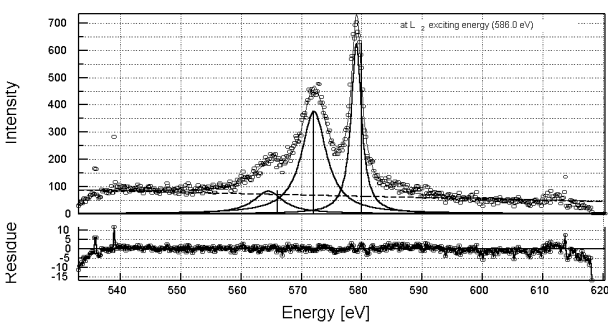
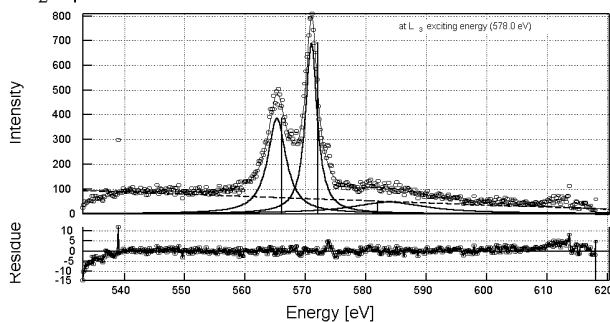
Cr metal



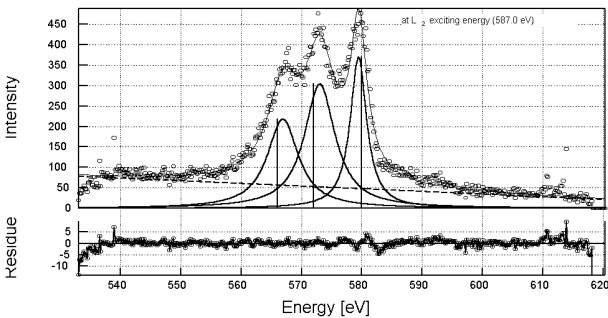
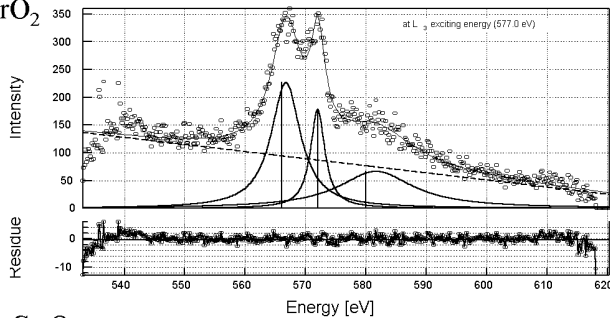
Cr₂O₃



FeCr₂O₄



CrO₂



K₂Cr₂O₇

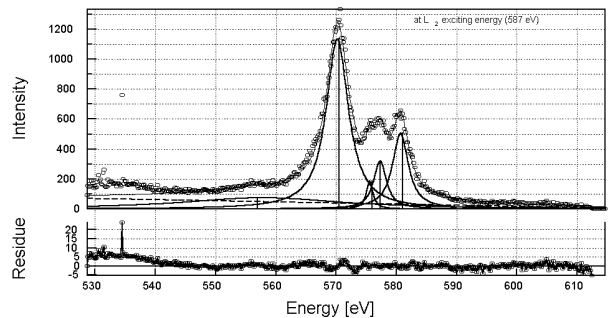
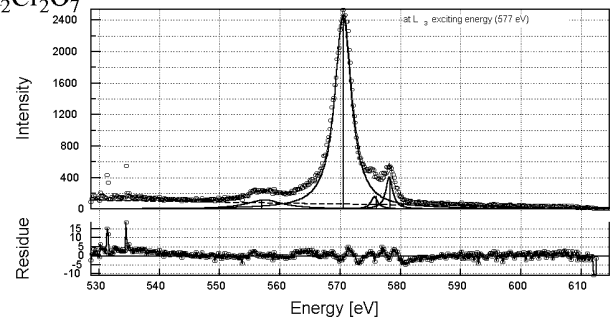


Figure 2 The Cr 2p x-ray fluorescence spectra in the Cr compounds at threshold energies